

PTO 03-1742

CY=JP DATE=19970304 KIND=WO
PN=98-20396

POLYMERIZED TONER AND METHOD OF MANUFACTURE THEREOF
[JUGO TONA- OYOBI SONO SEIZO HOHO]

Tokudai Ogawa, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. February 2003

Translated by: FLS, Inc.

PUBLICATION COUNTRY (10): WO

DOCUMENT NUMBER	(11): 9820396
DOCUMENT KIND	(12): A1
PUBLICATION DATE	(43): 19980514
APPLICATION NUMBER	(21): PCT/JP97/03972
APPLICATION DATE	(22): 19971031
ADDITION TO	(61):
INTERNATIONAL CLASSIFICATION	(51): G03G 0/093
DOMESTIC CLASSIFICATION	(52):
PRIORITY COUNTRY	(33):
PRIORITY NUMBER	(31): JP08310091
PRIORITY DATE	(32): 19961106
INVENTOR	(72): OGAWA, TOKUDAI, ET AL.
APPLICANT	(71): NIPPON ZEON CO., LTD.
TITLE	(54): POLYMERIZED TONER AND METHOD OF MANUFACTURE THEREOF
FOREIGN TITLE	[54A]: JUGO TONA- OYOBI SONO SEIZO HOHO

Polymerized Toner and Method of Manufacture Thereof

<Technical Field>

The present invention relates to a polymerized toner and a method of manufacture thereof, and more particularly, to a polymerized toner used for developing an electrostatic latent image formed by an electrophotographic method, electrostatic recording method, or the like, and a method of manufacture thereof. The present invention also relates to an image forming method comprised by using such a polymerized toner, and an image forming apparatus provided with the polymerized toner.

<Background Art>

In the electrophotographic method or electrostatic recording method, two-component developers comprising a toner and carrier particles, and one-component developers comprising substantially a toner alone and making no use of any carrier particles are known as developers for making electrostatic latent images visible. The one-component developers include magnetic one-component developers containing magnetic powder, and non-magnetic one-component developers containing no magnetic powder. In the non-magnetic one-component developers, a flowability improver, such as colloidal silica, is often added independently in order to improve the flowability of the toner. As the toner, there normally are used colored particles obtained by dispersing a colorant, such as carbon black, and other additives in a binder resin and granulating this.

Methods for manufacturing a toner are roughly divided into a grinding method and a polymerization method. In the grinding method, a synthetic resin, a colorant and, as needed, other additives are melted and mixed, this is ground and then classified so as to obtain particles having a desired particle diameter, and a toner is obtained. In the polymerization method, a polymerizable monomer composition is prepared by uniformly dissolving or dispersing a colorant, a polymerization initiator and, as needed, various additives, such as a crosslinking agent and a charge control agent, in a polymerizable monomer, the polymerizable monomer composition is dispersed in an aqueous dispersion medium containing a dispersion stabilizer by using a stirrer to form minute droplets of the polymerizable monomer composition, and the dispersion containing the minute droplets is subsequently heated to subject the droplets to suspension polymerization, a toner (polymerized toner) having a desired particle

/2

* Number in the margin indicates pagination in the foreign text.

diameter is obtained.

In either developer, an electrostatic latent image is actually developed with the toner. In an image forming apparatus, such as an electrophotographic apparatus or electrostatic recording apparatus, an electrostatic latent image normally is formed on a photosensitive member evenly charged, and a toner is applied to this electrostatic latent image to form a toner image (make the latent image visible), the toner image is transferred onto a transfer medium, such as transfer paper, and the unfixed toner image is then fixed to the transfer medium by various methods, such as heating, pressing, or use of solvent vapor. In the fixing step, the toner is often fusion-bonded to the transfer medium by passing the transfer medium, to which the toner image has been transferred, through a heating roll (fixing roll) and a press roll to fuse the toner to the transfer medium.

The details of images formed by an image forming apparatus, such as an electrophotographic copying machine, are required to be improved year by year. As a toner used in the image forming apparatus, a toner obtained by the grinding method has been mainly used in the past. The grinding method tends to form colored particles having a wide particle diameter distribution. In order for the toner to exhibit satisfactory developing characteristics, the ground product must be classified to adjust the particles so as to have a particle diameter distribution limited to a certain extent. However, classification itself is complicated and its yield is poor, and so the percent yield of the toner is reduced to a great extent. Therefore, a polymerized toner whose particle diameter is easy to control without conducting complicated manufacturing steps, such as classification, has come to receive attention in recent years. In the suspension polymerization method, a polymerized toner having desired particle diameter and particle diameter distribution can be obtained without grinding or classification. However, the conventional polymerized toners have problems because they cannot fully meet requirements in recent years, such as copying at higher speeds, the formation of full-color images, and energy savings.

/3

In recent years, copying machines, printers, and the like of an electrophotographic system have been required not only to reduce demand power, but also to achieve the copying or printing at higher speeds. A step in which energy is particularly consumed in the electrophotographic system is a fixing step conducted after transferring a toner from a photosensitive member onto a transfer medium, such as transfer paper. In the fixing step, the toner is fixed onto the transfer medium by heating and melting it. Therefore, a heating roll heated to a temperature of at least 150°C is used, and electric power is used as an energy source thereof. There is a demand for lowering the temperature of the heating roll from the viewpoint of energy savings. In order to decrease the

temperature of the heating roll, it is necessary to use a toner capable of being fixed at a temperature lower than in the past. That is, it is necessary to decrease the fixing temperature of the toner itself. The use of the toner capable of fixing at a temperature lower than that in the past permits lowering the temperature of the heating roll, and on the other hand, shortening the fixing time when the temperature of the heating roll is not lowered very much. Therefore, such a toner can meet the copying and printing at higher speeds.

In order to meet requirements, such as energy savings and copying at faster speeds, from the image forming apparatus in the design of a toner, it is only necessary to decrease the glass transition temperature of a binder resin making up the toner. When a toner is made up of a binder resin having a low glass transition temperature, however, the toner becomes poor in the so-called shelf-life stability because particles themselves of the toner tend to undergo blocking during storage or shipment, or in a toner box of an image forming apparatus, to aggregate.

In recent years, there has been a demand for formation of bright images in color copying or color printing by the electrophotographic system.

For example, in the full-color copying, the mere melting and softening of toners in a fixing step to fusion-bond the toners to a transfer medium are not enough, but it is necessary to uniformly melt and mix /4 the toners of different colors to mix their colors. In particular, since color images have come to be often used in OHP (overhead projector) sheets for presentations in various meetings or conferences, toner images fixed to such OHP sheets have been required to permit the formation of bright or clear images on a screen by permeating the sheets, i.e. have excellent permeability through the OHP. In order to satisfy the excellent permeability through the OHP, it is necessary for the toners to uniformly melt on a transparent OHP sheet made of a synthetic resin. Therefore, the melt viscosity of each toner at about the fixing temperature thereof must be designed lower than with conventional toners. Means for lowering the melt viscosity of the toner include a method in which the molecular weight or glass transition temperature of a binder resin used is lower than the binder resins for the conventional toners. In either method, however, the toner becomes poor in shelf-life stability because the toner tends to undergo blocking.

As a method for obtaining a polymerized toner having excellent fixing ability, it has been proposed in, for example, the publication of Tokkai No. 3-136065 to subject a polymerizable monomer containing a colorant and a charge control agent to suspension polymerization in the presence of a macromonomer. The macromonomer is a relatively long-chain linear molecule having a polymerizable functional group, for example, a group containing an unsaturated bond, such as a carbon-carbon double bond, at its molecular chain terminal. In this method, the macromonomer is

incorporated as a monomer unit into the molecular chain of a polymer thus formed. Hence, many branches attributable to the long-chain linear molecule of the macromonomer are generated in the molecular chain of the polymer. The polymer thus formed apparently becomes a high molecular weight polymer due to entanglement of the branches, i.e., the so-called physical crosslinking, so the offset resistance of the toner is improved. Meanwhile, the physical crosslinking by the macromonomer component is different from a chemical crosslinking using a crosslinking monomer, such as divinylbenzene and its crosslinked structure is relaxed; hence, the crosslinked structure collapses readily by heating. Accordingly, this polymerized toner is easily melted upon fixing using a heating roll and thus has an excellent fixing ability. However, the polymerized toner tends to undergo aggregation among toner particles during storage, and thus is unsatisfactory from the viewpoint of shelf-life stability. /5

In the conventional methods for lowering the fixing temperature of a toner and improving the uniformly melting ability thereof, as described above, an adverse correlation that the fixing ability of the resulting toner is improved, but its shelf-life stability is lowered arises. As a means for solving this adverse correlation, there has been proposed the so-called capsule type toner in which a toner made up of a binder resin having a low glass transition temperature is covered with a polymer having a high glass transition temperature, thus improving the blocking resistance of the toner to solve the problem of shelf-life stability.

As a method of manufacture of the capsule type toner, for example, in the publication of Tokkai No. 60-173552 has been proposed a method in which a coating layer composed of a colorant, magnetic particles or a conductive agent, and a binder resin is formed on each surface of spherical core particles having a minute particle size by means of a jet mill. As the core particles, particles formed of a thermoplastic transparent resin, such as an acrylate resin or styrene resin, are used. In this publication, it has been reported that in this method, a toner of multi-layer structure, which has excellent flowability and improved functional characteristics, can be obtained. When core particles having a low glass transition temperature are used in this method, however, the core particles themselves tend to undergo aggregation. In addition, in this method, the coating thickness of the binder resin is liable to thicken. Therefore, in this method, it is difficult to provide a toner improved in both fixing ability and uniformly melting ability while retaining its good shelf-life stability.

In the publication of Tokkai No. 2- 259657 has been proposed a method for manufacturing a toner for electrophotography, in which crosslinked toner particles prepared by suspension polymerization are added to a solution with an encapsulating polymer, a charge control agent and a parting /6

agent dissolved in an organic solvent, and a poor solvent is then added to the resultant mixture to form a coating film of the encapsulating polymer containing the charge control agent and parting agent on the surfaces of the crosslinked toner particles. In this method, however, it is difficult to obtain spherical particles because the solubility of the encapsulating polymer is reduced by the addition of the poor solvent to deposit the polymer on the surfaces of the crosslinked toner particles. The capsule walls formed on the surfaces of the crosslinked toner particles in this method are uneven in thickness, and moreover, are relatively thick. As a result, the effects for improving the development properties and fixing ability become insufficient.

In the publication of Tokkai No. 57-45558 has been proposed a method for manufacturing a toner for developing electrostatic latent images, in which core particles formed by polymerization are mixed with and dispersed in a 1 to 40 wt. % aqueous latex solution, and a water-soluble inorganic salt is then added to the dispersion to form a coating layer formed of fine particles obtained by emulsion polymerization on the surfaces of the core particles. However, in this method, there is a drawback because the temperature and humidity dependence of charge properties of the resultant toner becomes great due to the influence of a surfactant and the inorganic salt remaining on the fine particles, and the charge properties deteriorate under high-temperature and high-humidity conditions in particular.

In the publication of Tokkai No. 61-118758 is disclosed a method for manufacturing a toner, in which a composition containing a vinyl monomer, a polymerization initiator and a colorant is subjected to suspension polymerization to obtain core particles, and another vinyl monomer capable of providing a polymer having hydrophilicity at least equal to that of the resin contained in the core particles and a glass transition temperature higher than that of said resin is polymerized in the presence of the core particles to form a shell on each of the core particles. In this publication is also disclosed a parting agent, such as low molecular weight polyethylene, carnauba wax or silicone oil, that may be added to the core particles for preventing parting of the melted toner from adhering to the surface of a fixing roll. In this method, however, the vinyl monomer for forming the shell results in being adsorbed on each of the core particles and grow so that in many cases, it may be difficult to create a clear core-shell structure because the vinyl monomer absorbed in the interior 17 of the core particles is polymerized. Therefore, in this method, it is difficult to provide a toner sufficiently improved in shelf-life stability. In addition, in order to create a clear core-shell structure to improve the shelf-life stability, it has been necessary to increase the thickness of the shell.

In the publication of Tokkai No. 7-128908 is disclosed a method for directly manufacturing a polymerized toner by subjecting a monomer

composition containing a polymerizable monomer, a colorant and a parting agent to suspension polymerization in an aqueous medium, and a method comprising the steps containing the parting agent in a proportion of 10 to 40 parts by weight per 100 parts by weight of the polymerizable monomer and for removing the parting agent on the surface of the toner formed after completion of the polymerization step. In this method, when a polymer having a polar group is added to the monomer to polymerize the monomer, a core-shell structure is formed because the polar polymer gathers on each surface layer of polymer particles formed. In addition, the parting agent on the surface of the toner is removed, so staining due to attachment of the parting agent (wax) to a developing drum, a photosensitive drum, a transfer drum, or the like can be reduced. However, this method cannot fully improve the shelf-life stability, fixing temperature and the like of the toner and easily causes fogging, deterioration of image density, etc.

<Disclosure of the Invention>

An object of the present invention is to obtain a polymerized toner which has a low fixing temperature and uniformly melting ability, and is excellent in shelf-life stability (blocking resistance) and hardly causes fogging, deterioration of image density, etc., and a method of manufacture thereof.

Another object of the present invention is to provide a polymerized toner which can meet copying or printing at higher speeds, the formation of full-color images, and energy saving, and a method of manufacture thereof. /8

Yet another object of the present invention is to provide a polymerized toner capable of forming a toner image which exhibits excellent permeability (permeability through an OHP) when conducting printing on an OHP sheet with the toner and fixing the resulting image thereof, and a method of manufacture thereof.

Still another object of the present invention is to provide a polymerized toner which has excellent offset resistance, shelf-life stability and flowability, can meet high-speed printing at a low fixing temperature, can achieve high resolution and is suitable for use as a color toner, and a method of manufacture thereof.

As a result of painstaking research in order to overcome the above-mentioned problems in the aforesaid prior art, the inventors of the present invention conceived of a polymerized toner of core-shell structure, in which each of the core particles composed of colored polymer particles, which comprise a polyfunctional ester compound formed of a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic

acid, and a colorant, is covered with a shell formed of a polymer having a glass transition temperature higher than that of a polymer component making up the core particles.

This polymerized toner can be suitably produced by subjecting a composition containing the polyfunctional ester compound, the colorant and a polymerizable monomer capable of forming a polymer having a glass transition temperature of 80°C or lower to suspension polymerization, preferably, in the presence of a macromonomer to prepare colored polymer particles, and then using the colored polymer particles as core particles to subject another polymerizable monomer capable of forming a polymer having a glass transition temperature higher than that of the polymer component making up the core particles to suspension polymerization in the presence of the core particles, thus forming shell which is formed of a polymer layer and covers each of the core particles.

In the polymerized toner of the present invention, the core particles containing the polyfunctional ester compound and the polymer component having a lower glass transition temperature permit lowering the fixing temperature of the toner, also improving the uniformly melting ability, meeting requirements, such as the copying or printing at higher speeds, the formation of full-color images and good permeability through an OHP, and further forming a high-quality image because it is difficult for fogging, deterioration of image density, and the like to occur. On one hand, in the polymerized toner of the present invention, each of the core 19 can be covered with the thin shell, so the toner can exhibit good shelf-life particles stability (blocking resistance) and moreover fully meet various requirements, such as fixing ability and uniformly melting ability.

This had led them to completing the present invention on the basis of these findings.

Thus, in the present invention, a polymerized toner of core-shell structure, comprising core particles composed of colored polymer particles, which comprise a polyfunctional ester compound formed of a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, and a colorant, and shell which is formed of a polymer having a glass transition temperature higher than that of a polymer component making up the core particles and covers each of the core particles is provided.

In the present invention, a method for manufacturing a polymerized toner of core-shell structure, which comprises the steps of (1) subjecting a polymerizable monomer composition containing a polyfunctional ester compound formed from a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, a colorant, and a polymerizable monomer for the core, which is capable of forming a polymer having a glass transition temperature of 80°C or lower, to suspension polymerization in an aqueous

dispersion medium containing a dispersing agent to prepare core particles formed of colored polymer particles and then (2) subjecting a polymerizable monomer for the shell, which is capable of forming a polymer having a glass transition temperature higher than that of a polymer component making up the core particles, to suspension polymerization in the presence of the core particles, thus forming the shell which is formed of a polymer layer and covers each of the core particles is provided.

In the present invention, an image forming method comprising the steps of applying a toner to the surface of a photosensitive member, on which an electrostatic latent image has been formed, to make the latent image visible, and then transferring the visible image onto a transfer medium; said image forming methods characterized by the above-mentioned polymerized toner of core-shell structure being used as the toner is /10 provided.

In the present invention, an image forming apparatus, comprising a photosensitive member, a means for charging the surface of the photosensitive member, a means for forming an electrostatic latent image on the surface of the photosensitive member, a means for receiving a toner, a means for supplying the toner to develop the electrostatic latent image on the surface of the photosensitive member, thereby forming a toner image, and a means for transferring the toner image from the surface of the photosensitive member to a transfer medium; said image forming apparatus characterized by the means for receiving the toner containing the above-mentioned polymerized toner of core-shell structure is obtained.

<Brief Description of the Drawings>

Figure 1 is a cross section showing an example of an image forming apparatus to which a polymerized toner in the present invention is applied.

<Best Mode for Carrying out the Invention>

The polymerized toner in the present invention is a polymerized toner with a core-shell structure comprising core particles and a shell which covers each of the core particles. The polymerized toner in the present invention can be produced by polymerizing a polymerizable monomer for the shell in the presence of core particles. The core particles comprise, as essential components, a polyfunctional ester compound formed from a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, and a colorant in a polymer component (binder resin). The glass transition temperature of a polymer component making up the shell is higher than that of the polymer component making up the core particles.

Polyfunctional Ester Compound

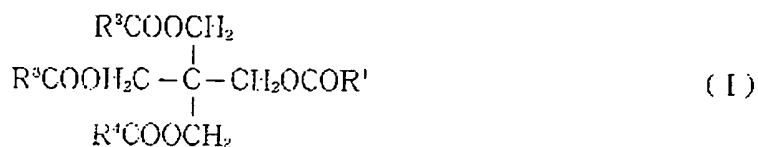
The polyfunctional ester compound used in the present invention is an ester formed of a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid.

examples of the trifunctional or higher polyfunctional polyhydric alcohol include aliphatic alcohols, such as glycerol, pentaerythritol and pentaglycerol; alicyclic alcohols, such as phloroglucitol, quercitol and inositol; aromatic alcohols, such as tris-(hydroxymethyl)benzene; saccharides, such as D-erythrose, L-arabinose, D-mannose, D-galactose, D-fructose, L-rhamnose, saccharose, maltose and lactose; and sugar alcohols, such as erythritol, D-threitol, L-arabitol, adonitol and xylitol. Of these, pentaerythritol is preferred. /11

examples of the carboxylic acid include aliphatic carboxylic acids, such as acetic acid, butyric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, stearic acid, margaric acid, arachidic acid, cerotic acid, melissic acid, erucic acid, brassidic acid, sorbic acid, linolic acid, linolenic acid, behenolic acid, tetrolic acid and ximenynic acid; alicyclic carboxylic acids, such as cyclohexanecarboxylic acid, hexahydroisophthalic acid, hexahydroterephthalic acid and 3,4,5,6-tetrahydrophthalic acid; and aromatic carboxylic acids such as benzoic acid, toluic acid, cuminic acid, phthalic acid, isophthalic acid, terephthalic acid, trimesic acid, trimellitic acid and hemimellitic acid. Of these, carboxylic acids having, preferably, 10 to 30 carbon atoms, and more preferably, 13 to 25 carbon atoms are preferred, and aliphatic carboxylic acids having this number of carbon atoms are more preferred. Among the aliphatic carboxylic acids, stearic acid and myristic acid are particularly preferred.

In the polyfunctional ester compound used in the present invention, the carboxylic acids reacting with at least three (3) functional groups (OH groups) of the polyhydric alcohol to form respective ester bonds may be the same or different from each other. When the kinds of the carboxylic acids reacting with the polyhydric alcohol are different from each other, it is desirable that a difference between the maximum value and the minimum value of the number of carbon atoms among the carboxylic acids be preferably at most 9, and more preferably, at most 5. /12

The polyfunctional ester compound is preferably a compound represented by the formula (I):



(Where R^1 , R^2 , R^3 and R^4 are an alkyl group or phenyl group, respectively, and the number of carbon atoms in the alkyl group or phenyl group is preferably 10 to 30, and more preferably, 13 to 25.)

Pentaerythritol tetrastearate [a compound in which R^1 , R^2 , R^3 and R^4 in the formula (I) are all $\text{CH}_3(\text{CH}_2)_{16}$ groups], pentaerythritol tetramyristate [a compound in which R^1 , R^2 , R^3 and R^4 in the formula (I) are all $\text{CH}_3(\text{CH}_2)_{12}$ groups], glycerol triarachidate, and the like can be cited as specific examples of the polyfunctional ester compound. The polyfunctional ester compound is preferably easily soluble in a polymerizable monomer for the core.

The polyfunctional ester compound normally is used in a proportion of 0.1 to 40 parts by weight, preferably, 1 to 20 parts by weight, and more preferably, 3 to 15 parts by weight per 100 parts by weight of a polymer component making up core particles or a monomer for forming the polymer component (polymerizable monomer for the core). The proportion of the polyfunctional ester compound used falls within the above-mentioned range; hence, a polymerized toner, which has a low fixing temperature and uniformly melting ability, and is excellent in shelf-life stability (blocking resistance) and hardly causes fogging, deterioration of image density, etc., can be provided. If the proportion of the polyfunctional ester compound used is too low, its effect is reduced. If the proportion is too high on the other hand, it is difficult to form the core particles, and the shelf-life stability of the resulting polymerized toner also deteriorates. /13

Colorant

Dyes and pigment, such as carbon black, titanium white, Nigrosine Base, aniline blue, Chalcoil Blue, chrome yellow, ultramarine blue, Orient Oil Red, Phthalocyanine Blue and Malachite Green oxalate; and magnetic powders such as cobalt, nickel, diiron trioxide, triiron tetroxide, manganese iron oxide, zinc iron oxide and nickel iron oxide can be cited as examples of the colorant used in the present invention.

C.I. Direct Red 1, C.I. Direct Red 4, C.I. Acid Red 1, C.I. Basic Red 1, C.I. Mordant Red 30, C.I. Direct Blue 1, C.I. Direct Blue 2, C.I. Acid Blue 9, C.I. Acid Blue 15, C.I. Basic Blue 3, C.I. Basic Blue 5,

C.I. Mordant Blue 7, C.I. Direct Green 6, C.I. Basic Green 4, C.I. Basic Green 6, and the like can be cited as examples of colorants for magnetic color toners. Chrome yellow, cadmium yellow, Mineral Fast Yellow, Navel Yellow, Naphthol Yellow S, Hansa Yellow G, Permanent Yellow NCG, Tartrazine Lake, chrome orange, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Benzidine Orange, cadmium red, Permanent Red 4R, Watchung Red Calcium salt, eosine lake, Brilliant Carmine 3B, manganese violet, /14 Fast Violet B, Methyl Violet Lake, iron blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue BC, chrome green, chromium oxide, Pigment Green B, Malachite Green Lake, Final Yellow Green G, and the like can be cited as examples of pigments for magnetic color toners.

C.I. Pigment Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 39, 40, 41, 48, 49, 50, 51, 52, 53, 54, 55, 57, 58, 60, 63, 64, 68, 81, 83, 87, 88, 89, 90, 112, 114, 122, 123, 163, 202, 206, 207 and 209; C.I. Pigment Violet 19; C.I. Vat Red 1, 2, 10, 13, 15, 23, 29 and 35, and the like are cited as examples of magenta color pigments for full-color toners.

Oil-soluble dyes, such as C.I. Solvent Red 1, 3, 8, 23, 24, 25, 27, 30, 49, 81, 82, 83, 84, 100, 109 and 121; C.I. Disperse Red 9; C.I. Solvent Violet 8, 13, 14, 21 and 27; and C.I. Disperse Violet 1; basic dyes such as C.I. Basic Red 1, 2, 9, 12, 13, 14, 15, 17, 18, 22, 23, 24, 27, 29, 32, 34, 35, 36, 37, 38, 39 and 40; C.I. Basic Violet 1, 3, 7, 10, 14, 15, 21, 25, 26, 27 and 28, and the like are cited as examples of magenta dyes for full-color toners.

C.I. Pigments Blue 2, 3, 15, 16 and 17; C.I. Vat Blue 6; C.I. Acid /15 Blue 45; copper phthalocyanine dyes with 1 to 5 phthalimidomethyl groups added to a phthalocyanine skeleton, and the like are cited as examples of cyan color pigments for full-color toners.

C.I. Pigment Yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 15, 16, 17, 23, 65, 73, 83 and 138; C.I. Vat Yellow 1, 3 and 20, and the like are cited as examples of yellow color pigments for full-color toners.

These dyes or pigments normally are used in a proportion of 0.1 to 20 parts by weight, and preferably, 1 to 10 parts by weight per 100 parts by weight of the polymer component making up the core particles or the polymerizable monomer for the core. The magnetic powder normally is used in a proportion of 1 to 100 parts by weight, and preferably, 5 to 50 parts by weight per 100 parts by weight of the polymer component making up the core particles or the polymerizable monomer for the core.

Core Particles

The core particles used in the present invention containing, as a polymer component (binder resin), a (co)polymer of a vinyl monomer, such as a polyester resin, or a (meth)acrylic ester-styrene copolymer. As the polymer component for the core particles, the (meth)acrylic ester-styrene copolymer is preferred because it is easy to form particles by polymerization and control the glass transition temperature of the polymer component.

In the polymerized toner in the present invention, the volume average particle diameter (d_v) of the core particles is normally 0.5 to 20 μm , and preferably 1 to 10 μm . If the core particles are too large, the resolution of an image formed with such a toner tends to decrease. The ratio (d_v)/(d_p) of the volume average particle diameter (d_v) to a number average particle diameter (d_p) in the core particles is normally at most 1.7, and preferably, at most 1.5. If this ratio is too high, the resolution of an image formed with such a toner tends to decrease.

/16

No particular restrictions are imposed on the method of manufacture of the core particles used in the present invention, and either an emulsion polymerization, suspension polymerization, precipitation polymerization and soap-free polymerization may be used. However, a method in which a polymerizable monomer for the core is subjected to suspension polymerization is preferred because the polyfunctional ester compound and colorant can be uniformly contained in each of core particles thus formed, and the fixing ability of the resulting toner is improved.

The polymerizable monomer for the core used in the present invention is such that a polymer having a glass transition temperature of generally 80°C or lower, preferably, 10 to 70°C, and more preferably, 15 to 60°C can be formed. The polymerizable monomer for the core can be used by combining one of such monomers or by combining at least two (2) of them. If the glass transition temperature of a polymer comprising the polymerizable monomer for the core is too high, its fixing temperature increases, the permeability through an OHP decreases, and it cannot suit faster copying or printing.

The glass transition temperature (T_g) of the polymer is a calculated value (referred to as calculated T_g) calculated out in the kind(s) and proportion(s) of monomer(s) used. When the monomer used is of one kind, the T_g of a homopolymer formed from this monomer is defined as the T_g of the polymer in the present invention. For example, the T_g of polystyrene is 100°C. Therefore, when styrene is used as a monomer by itself, the monomer can be said to form a polymer having a T_g of 100°C. When two or more monomers are used and the polymer formed is a copolymer, the T_g of the copolymer is calculated out in the kinds and proportions of the monomers used. For example, when 78 wt. % of styrene and 22 wt. % of

n-butyl acrylate are used as monomers, the monomers can be said to form a polymer having a **Tg** of 50°C because the **Tg** of a styrene-n-butyl acrylate copolymer formed at this monomer ratio is 50°C.

The definition of "a polymerizable monomer for the core, which /17
is capable of forming a polymer having a glass transition temperature of 80°C or lower" does not mean that when plural monomers are used, the individual monomers must form respective polymers having a **Tg** of 80°C or lower. When one monomer is used, the **Tg** of a homopolymer formed from the monomer must be 80°C or lower. When two or more monomers are used, however, it is only necessary for the **Tg** of a copolymer formed from the monomer mixture to be 80°C or lower. Therefore, those which separately form a homopolymer having a **Tg** higher than 80°C may be contained in the monomer mixture. For example, although the **Tg** of a styrene homopolymer is 100°C, styrene may be used as a component of the polymerizable monomer for the core so far as a copolymer having a **Tg** of 80°C or lower can be formed by using a mixture of styrene with a monomer (for example, n-butyl acrylate) which forms a homopolymer having a low **Tg**.

In the present invention, vinyl monomers normally are used as the polymerizable monomer for the core. Various kinds of vinyl monomers are used either singly or in combination of two or more thereof so as to adjust the **Tg** of the resulting polymer within the desired range.

Styrene-based monomers such as styrene, vinyltoluene and α -methylstyrene; acrylic acid and methacrylic acid; (meth)acrylic acid derivatives, such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dimethylaminoethyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dimethylaminoethyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide and methacrylamide; ethylenically unsaturated monoolefins such as ethylene, propylene and butylene; /18
vinyl halides, such as vinyl chloride, vinylidene chloride and vinyl fluoride; vinyl esters, such as vinyl acetate and vinyl propionate; vinyl ethers, such as vinyl methyl ether and vinyl ethyl ether; vinyl ketones, such as vinyl methyl ketone and methyl isopropenyl ketone; nitrogen-containing vinyl compounds, such as 2-vinylpyridine, 4-vinylpyridine and N-vinylpyrrolidone, and the like can be cited as examples of the vinyl monomers used in the present invention. These vinyl monomers may be used either singly or by combining a plurality of them. Of these, the styrene-based monomers, or the (meth)acrylic acid derivatives are suitably used as a polymerizable monomer for the core.

Of these, a combination of a styrene-based monomer with a (meth)acrylic acid derivative is preferably used as the polymerizable monomer for the core. Combinations of styrene with butyl acrylate (i.e., n-butyl acrylate), and styrene with 2-ethylhexyl acrylate can be cited for particularly

preferable specific examples thereof.

It is preferable from the viewpoint of improving the shelf-life stability and offset resistance of the resulting polymerized toner to use a crosslinking monomer in combination with the polymerizable monomer for the core composed of the vinyl monomer(s). Aromatic divinyl compounds, such as divinylbenzene, divinyl naphthalene and derivatives thereof; diethylenic esters of unsaturated carboxylic acids, such as ethylene glycol dimethacrylate and diethylene glycol dimethacrylate; divinyl compounds, such as N,N-divinylaniline and divinyl ether; compounds having at least three vinyl groups, and the like can be cited as examples of the crosslinking monomer.

These crosslinking monomers may be used either singly or by combining at least 2 of them. It is desirable that the crosslinking monomer be used in a proportion of normally 0.1 to 5 parts by weight, and preferably, 0.3 to 2 parts by weight per 100 parts by weight of the polymerizable monomer for the core. /19

In the present invention, a macromonomer is preferably copolymerized with the polymerizable monomer for the core from the viewpoint of improving the balance between the shelf-life stability and the fixing ability of the resulting polymerized toner. In order to copolymerize the macromonomer, it is only necessary to polymerize a polymerizable monomer composition containing the polyfunctional ester compound, the colorant and the polymerizable monomer for the core in the presence of the macromonomer to synthesize colored polymer particles (core particles). In fact, it is preferable that the macromonomer be contained in the polymerizable monomer composition to conduct suspension polymerization.

The macromonomer (also referred to as macromer) is a relatively long-chain linear molecule having a polymerizable functional group (for example, a group containing an unsaturated bond such as a carbon-carbon double bond) at its molecular chain terminal. The macromonomer is preferably an oligomer or polymer having a polymerizable vinyl functional group at its molecular chain terminal and a number average molecular weight of normally 1,000 to 30,000. If a macromonomer having a low number average molecular weight is used, the surface part of the resulting polymerized toner becomes soft, and its shelf-life stability shows a tendency to deteriorate. If a macromonomer having a high number average molecular weight is used on the other hand, the flowability of the macromonomer deteriorates, and the fixing ability and shelf-life stability decrease.

Examples of the polymerizable vinyl functional group which the macromonomer has at its molecular chain terminal include an acryloyl group and a methacryloyl group. The methacryloyl group is suitable from the viewpoint of ease of copolymerization.

The macromonomer used in the present invention preferably has a glass transition temperature higher than that of a polymer obtained by polymerizing the polymerizable monomer for the core. A difference in the **T_g** between the polymer obtained by polymerizing the polymerizable monomer /20 for the core and the macromonomer is relative. For example, when the polymerizable monomer for the core is such that it forms a polymer having a **T_g** of 80°C, it is only necessary for the macromonomer to have a **T_g** higher than 80°C. When the polymerizable monomer for the core is such that it forms a polymer having a **T_g** of 50°C, the macromonomer may also be one having a **T_g** of, for example, 60°C. The **T_g** of the macromonomer is a value measured by means of an ordinary measuring device such as a DSC.

Polymers obtained by polymerizing styrene, styrene derivatives, methacrylic esters, acrylic esters, acrylonitrile and methacrylonitrile either singly or by combining two or more monomers thereof; macromonomers having a polysiloxane skeleton; those disclosed in Tokkai No. 3-203746 on pages 4 to 7, and the like can be cited as specific examples of the macromonomer used in the present invention.

Of these macromonomers, hydrophilic macromonomers, and in particular, polymers obtained by polymerizing methacrylic esters or acrylic esters either singly or by combining two or more monomers thereof are preferred in the present invention.

The amount of the macromonomer used normally is 0.01 to 10 parts by weight, preferably, 0.03 to 5 parts by weight, and more preferably, 0.05 to 1 part by weight per 100 parts by weight of the polymerizable monomer for the core. If the amount of the macromonomer used is too low, the shelf-life stability decreases. If the amount of the macromonomer is too high, the fixing ability decreases.

In the present invention, it is preferable that the core particles be obtained by subjecting the polymerizable monomer for the core, the macromonomer and, as needed, the crosslinking monomer to suspension polymerization.

The suspension polymerization normally is performed in an aqueous dispersion medium containing a dispersing agent. More specifically, the suspension polymerization is conducted by mixing a polymerizable /21 monomer (vinyl monomer) for the core, a polyfunctional ester compound, a colorant, a macromonomer, and as needed, a crosslinking monomer, a radical polymerization initiator and other additives, uniformly dispersing them by means of a ball mill or the like to prepare a liquid mixture (polymerizable monomer composition), pouring the liquid mixture into an aqueous dispersion medium containing a dispersing agent, dispersing the liquid mixture in the dispersion medium by means of a mixer having high shearing force to

form minute droplets, and then subjecting them to suspension polymerization at a temperature of generally 30 to 200°C.

The dispersing agent preferably used in the present invention is a colloid of a hardly water-soluble metallic compound. Sulfates, such as barium sulfate and calcium sulfate; carbonates, such as barium carbonate, calcium carbonate and magnesium carbonate; phosphates, such as calcium phosphate; metal oxides, such as aluminum oxide and titanium oxide; metal hydroxides, such as aluminum hydroxide, magnesium hydroxide and ferric hydroxide, and the like can be cited as examples of the hardly water-soluble metallic compound. Of these, colloids of hardly water-soluble metal hydroxides are preferred because the particle diameter distribution of the polymer particles can be narrowed, and the brightness or sharpness of an image formed from such a polymerized toner is enhanced.

The colloid of the hardly water-soluble metal hydroxide is not limited by the method of manufacture thereof. However, a colloid of a hardly water-soluble metal hydroxide obtained by adjusting the pH of an aqueous solution of a water-soluble polyvalent metallic compound to 7 or higher, in particular, a colloid of a hardly water-soluble metal hydroxide formed by reacting a water-soluble polyvalent metallic compound with an alkali metal hydroxide in an aqueous phase is preferred. This colloid is used as an aqueous dispersion.

The colloid of the hardly water-soluble metal hydroxide used in the present invention preferably has number particle diameter distributions, D_{50} (50% cumulative value of number particle diameter distribution) of at most 0.5 μm and D_{90} (90% cumulative value of number particle diameter distribution) of at most 1 μm . If the particle diameter of the colloid is too large, the stability of the suspension polymerization collapses, and the shelf-life stability of polymerized toner decreases.

The dispersing agent normally is used in a proportion of 0.1 to 22 20 parts by weight per 100 parts by weight of the monomer for the core.

If the amount of the dispersing agent used is too low, it is difficult to achieve sufficient polymerization stability, so the polymer tends to aggregate. If the amount of the dispersing agent used is too high on the other hand, the effect of the dispersing agent on polymerization stability is saturated, which is uneconomical. In addition, the viscosity of the aqueous dispersion medium becomes too high, so it is difficult to form fine droplets of the liquid mixture.

In the present invention, a water-soluble polymer may be used as a dispersing agent, as needed. Polyvinyl alcohol, methyl cellulose gelatin examples of the water-soluble polymer, and the like can be exemplified as examples of the water-soluble polymer. In the present invention, there is no need to use any surfactant. However, a surfactant may be used for

the purpose of stably conducting the suspension polymerization so far as the dependence of the charge properties of polymerized toner on environment does not increase.

Water-soluble polymerization initiators, such as persulfates, such as potassium persulfate and ammonium persulfate; and azo compounds such as 4,4'-azobis(4-cyanovaleric acid), 2-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis-2-methyl-N-1,1-bis-(hydroxymethyl)-2-hydroxyethylpropionamide, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitrile and 1,1'-azobis(1-cyclohexanecarbonitrile); and oil-soluble polymerization initiators like peroxides, such as methyl ethyl peroxide, di-t-butyl peroxide, acetyl peroxide, dicumyl peroxide, lauroyl peroxide, benzoyl peroxide, t-butyl peroxy-2-ethylhexanoate, di-isopropyl peroxydicarbonate and di-t-butyl peroxyisophthalate, can be exemplified as examples of the radical polymerization initiator. Redox initiators composed of combinations of these polymerization initiators with a reducing agent may also be mentioned. /23

Of these radical polymerization initiators, the oil-soluble radical initiators are preferred, with oil-soluble radical initiators selected from among organic peroxides whose ten-hour half-life temperatures are 60 to 80°C, and preferably, 65 to 80°C, and whose molecular weights are 250 or lower being particularly preferred. Of the oil-soluble radical initiators, t-butyl peroxy-2-ethylhexanoate and t-butyl peroxyneodecanoate are particularly preferred because the resulting polymerized toner scarcely gives odor upon printing and barely causes environmental destruction by volatile components, such as odor.

The amount of the polymerization initiator used normally is 0.001 to 3 wt. % based on the aqueous medium. If the amount of the polymerization initiator used is less than 0.001 wt. %, the rate of polymerization becomes slow. If the amount exceeds 3 wt. %, particles having a particle diameter smaller than 1 μ m are formed as a by-product. Therefore, it is not preferable to use the initiator in such a little or great amount.

In the present invention, as needed, various kinds of additives, such as a molecular weight modifier, may be used by mixing them with the polymerizable monomer for the core.

examples of the molecular weight modifier include mercaptans, such as t-dodecylmercaptan, n-dodecylmercaptan and n-octylmercaptan; and halogenated hydrocarbons, such as carbon tetrachloride and carbon tetrabromide. The molecular weight modifier may be added before the initiation of the polymerization or in the course of the polymerization. The molecular weight modifier is used in a proportion of generally 0.01 to 10 parts by weight, and preferably, 0.1 to 5 parts by weight per 100 parts by weight of the polymerizable monomer for the core.

In the polymerized toner of the present invention, the polyfunctional ester compound fulfills a function as a parting agent, and so it is not always necessary to use any other parting agent. However, a parting agent, for example, a low molecular weight polyolefin, such as low molecular weight polyethylene, low molecular weight polypropylene or low molecular weight polybutylene; a paraffin wax, and the like may be used within limits not impeding the objects of the present invention. /24

A lubricant, such as oleic acid or stearic acid; a dispersion aid, such as a silane or titanium coupling agent; and the like may also be used for the purpose of uniformly dispersing the colorant in the core particles, among other purposes. Such a lubricant or dispersion aid normally is used in a proportion of about 1/1,000 to 1/1 based on the weight of the colorant.

The polymerization for obtaining the core particles is continued until the conversion of the polymerizable monomer into a polymer reaches generally at least 80%, preferably at least 85%, and more preferably at least 90%. If the conversion into the polymer is lower than 80%, a large amount of the polymerizable monomer for the core remains unreacted, so that each surface of the resultant core particles is covered with a copolymer of the polymerizable monomer for the core and a polymerizable monomer for the shell even when the polymerizable monomer for the shell is added to conduct polymerization. Therefore, a difference in the **T_g** between the core particles and the shell becomes small, so the shelf-life stability of the polymerized toner tends to decrease.

Shell

In the present invention, the polymerized toner can be obtained by polymerizing a polymerizable monomer for the shell in the presence of the core particles.

The polymerizable monomer for the shell used in the present invention is one that can form a polymer having a glass transition temperature higher than that of the polymer component making up the core particles. A difference in the **T_g** between the polymer obtained by the polymerizable monomer for the shell and the polymer component making up the core particles is relative.

As the polymerizable monomer for the shell, monomers capable of forming a polymer having a glass transition temperature higher than 80°C, for example, styrene and methyl methacrylate, either singly or in combination of two or more monomers thereof can be used. When the glass transition temperature of the polymer component of the core particles is considerably lower than 80°C, the polymerizable monomer for the shell may be one /25 that forms a polymer having a glass transition temperature of 80°C or

lower. However, the glass transition temperature of the polymer formed from the polymerizable monomer for the shell must be preset so as to be higher than the glass transition temperature of the polymer component of the core particles. In order to improve the shelf-life stability of the polymerized toner, the glass transition temperature of the polymer formed from the polymerizable monomer for the shell is preset within a range of generally 50 to 120°C, preferably, 60 to 115°C, and more preferably, 80 to 110°C. If the glass transition temperature of the polymer formed from the polymerizable monomer for the shell is too low, the shelf-life stability of the polymerized toner may be lowered in some cases even if such a glass transition temperature is higher than that of the polymer component of the core particles. In many cases, the glass transition temperature of the polymer component of the core particles may be represented by the calculated **T_g** of a polymer formed from the polymerizable monomer for the core.

A difference in the glass transition temperature between the polymer formed from the polymerizable monomer for the core and the polymer formed from the polymerizable monomer for the shell normally is at least 10°C, preferably at least 20°C, and more preferably, at least 30°C.

The polymerizable monomer for the shell is preferably polymerized in the presence of the core particles after it is formed into droplets smaller than the number average particle diameter of the core particles in an aqueous dispersion medium. If the droplet diameter of the droplets of the polymerizable monomer for the shell is too large, the shelf-life stability of the resulting polymerized toner shows a tendency to decrease.

In order to form the polymerizable monomer for the shell into fine droplets, a mixture of the polymerizable monomer for the shell and the aqueous dispersion medium is subjected to a finely dispersing treatment by means of, for example, an ultrasonic emulsifier. It is preferred that the aqueous dispersion thus obtained be added to the reaction system in which the core particles are present.

The polymerizable monomer for the shell is not particularly limited by solubility in water at 20°C. However, a polymerizable monomer for the shell having a high solubility in water, specifically, a monomer having a solubility of at least 0.1 wt. % in water at 20°C /26 becomes liable to quickly migrate to the surfaces of the core particles, so a polymerized toner having good shelf-life stability is easy to obtain.

On the other hand, when a polymerizable monomer for the shell having a solubility lower than 0.1 wt. % in water at 20°C is used, its migration to the surfaces of the core particles becomes slow. Therefore, it is preferable to polymerize such a monomer after adding it in the form of fine droplets to the reaction system. Even when a polymerizable monomer for the shell

having a solubility lower than 0.1 wt. % in water at 20°C is used, the polymerizable monomer for the shell easily and quickly migrates to the surfaces of the core particles when an organic solvent having a solubility of at least 5 wt. % in water at 20°C is added to the reaction system, so a polymerized toner having good shelf-life stability is easily obtained.

examples of the polymerizable monomer for the shell having a solubility lower than 0.1 wt. % in water at 20°C include styrene, butyl acrylate, 2-ethylhexyl acrylate, ethylene, propylene, etc. examples of the polymerizable monomer for the shell having a solubility of at least 0.1 wt. % in water at 20°C include (meth)acrylic esters, such as methyl methacrylate and methyl acrylate; amides, such as acrylamide and methacrylamide; vinyl cyanide compounds, such as acrylonitrile and methacrylonitrile; nitrogen-containing vinyl compounds, such as 4-vinylpyridine; and vinyl acetate and acrolein.

Lower alcohols, such as methanol, ethanol, isopropyl alcohol, n-propyl alcohol and butyl alcohol; ketones, such as acetone and methyl ethyl ketone; cyclic ethers, such as tetrahydrofuran and dioxane; ethers, such as dimethyl ether and diethyl ether; amides, such as dimethylformamide, and the like can be cited as examples of an organic solvent preferably used in the case where the polymerizable monomer for the shell having a solubility lower than 0.1 wt. % in water at 20.degree. C. is used.

The organic solvent is added in such an amount that the /27
solubility of the polymerizable monomer for the shell in the dispersion medium (containing water and the organic solvent in combination) is at least 0.1 wt. %. The specific amount of the organic solvent added varies in the kind of the organic solvent, and the kind and amount of the polymerizable monomer for the shell. However, it normally is 0.1 to 50 parts by weight, preferably, 0.1 to 40 parts by weight, and more preferably, 0.1 to 30 parts by weight per 100 parts by weight of the aqueous dispersion medium. No particular restrictions are imposed on the order of addition of the organic solvent and the polymerizable monomer for the shell to the reaction system. In order to facilitate the migration of the polymerizable monomer for the shell to the core particles to make it easy to obtain a polymerized toner having good shelf-life stability, however, it is preferable to first add the organic solvent to the reaction system and then add the polymerizable monomer for the shell.

When a monomer having a solubility lower than 0.1 wt. % in water at 20°C and a monomer having a solubility of at least 0.1 wt. % in water at 20°C are used in combination, it is preferable to first add the monomer having a solubility of at least 0.1 wt. % in water at 20°C to polymerize it, then add the organic solvent, and further, add the monomer having a solubility lower than 0.1 wt. % in water at 20°C to polymerize it. In this adding method, the **Tg** of the polymer obtained from the polymerizable

monomer for the shell, which is polymerized in the presence of the core particles for the purpose of controlling the fixing temperature of the resulting polymerized toner, and the amount of the monomer added can be suitably controlled.

It is preferable to use various kinds of charge control agents in the polymerizable monomer for the shell. When a charge control agent is contained in the shell, the chargeability of the polymerized toner can be improved. Nigrosine NO1 (product of Orient Chemical Industries Ltd.), Nigrosine EX (product of Orient Chemical Industries Ltd.), Spiron Black TRH (product of Hodogaya Chemical Co., Ltd.), T-77 (product of Hodogaya Chemical Co., Ltd.), Bontron S-34 (product of Orient Chemical Industries Ltd.) and Bontron E-84 (product of Orient Chemical Industries Ltd.), and the like can be cited as specific examples of the charge control agents.

The charge control agent is used in a proportion of generally 0.01 to 10 parts by weight, and preferably, 0.1 to 5 parts by weight per 100 parts by weight of the polymerizable monomer for the core. /28

A method in which the polymerizable monomer for the shell is added to the reaction system of the polymerization reaction which has been conducted for obtaining the core particles, thereby continuously conducting polymerization, a method in which the core particles obtained in a separate reaction system are charged, to which the polymerizable monomer for the shell is added, thereby conducting polymerization stepwise, among other methods can be cited as examples of a specific method for polymerizing the polymerizable monomer for the shell in the presence of the core particles.

The polymerizable monomer for the shell may be added to the reaction system in one lot, or continuously or intermittently by means of a pump such as a plunger pump.

In order to make it easy to obtain polymer particles of core-shell structure, it is preferable to add a water-soluble radical initiator while the polymerizable monomer for the shell is being added. It is thought that when the water-soluble radical initiator is added upon the addition of the polymerizable monomer for the shell, the water-soluble initiator enters in the vicinity of each outer surface of the core particles to which the polymerizable monomer for the shell has migrated, so a polymer layer (shell) is easy to form on the core particle surface.

Persulfates, such as potassium persulfate and ammonium persulfate; azo initiators, such as 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(2-amidinopropane) dihydrochloride and 2,2'-azobis-2-methyl-N-1,1-bis-(hydroxymethyl)-2-hydroxyethylpropionamide; combinations of an oil-soluble initiator, such as cumene peroxide with a redox catalyst, and the like can be cited as examples of the water-soluble radical initiator. The amount of the water-soluble radical

initiator used normally is 0.001 to 1 wt. % based on the aqueous medium.

Polymerized Toner

/29

In the polymerized toner in the present invention, the weight ratio of the polymerizable monomer for the core to the polymerizable monomer for the shell normally is 40/60 to 99.9/0.1, preferably, 60/40 to 99.5/0.5, and more preferably 80/20 to 99/1. If the proportion of the polymerizable monomer for the shell is too low, there is little effect for improving the shelf-life stability. If the proportion is too high on the other hand, there are little effects for reducing the fixing temperature and improving the permeability through an OHP.

The polymerized toner of the present invention is composed of fine spherical particles sharp in a particle diameter distribution in which the volume average particle diameter normally is 2 to 20 μm , preferably, 3 to 15 μm , and the particle diameter distribution (volume average particle diameter/number average particle diameter) normally is at most 1.6, preferably, at most 1.5.

The polymerized toner of the present invention is composed of polymer particles of core-shell structure comprising the core particles and the shell which covers each of the core particles. In the polymerized toner with a core-shell structure of the present invention, the average thickness of the shell normally is 0.001 to 1 μm , preferably, 0.005 to 0.5 μm . If the shell is too thick, the fixing ability of the toner decreases. If it is too thin on the other hand, the shelf-life stability of the toner decreases. The particle diameters of the core particles and the thickness of the shell in the polymerized toner can be determined by directly measuring the size and shell thickness of each of particles selected at random from electron photomicrographs thereof when they can be observed through an electron microscope. If it is difficult to observe the particle diameters of the core particles and the thickness of the shell with an electron microscope, the particle diameters of the core particles are measured with the electron microscope in the same manner as described above or by means of a Coulter counter at the stage of formation of the core particles.

After the core particles are then covered with the shell, the particle diameters of the polymerized toner particles are measured again with the electron microscope or by means of the Coulter counter; hence, the average thickness of the shell can be found from changes in particle diameter before and after the covering with the shell. When it is difficult to measure the shell thickness by these methods, the thickness of the shell can be calculated out from the particle diameter of the core particles and the used amount of the polymerizable monomer for forming the shell. /30

The polymerized toner of the present invention contains toluene-insoluble matter in an amount of generally at most 50 wt. %, preferably,

at most 20 wt. %, and more preferably at most 10 wt. %. If the toluene-insoluble matter is contained in plenty, the fixing ability of the polymerized toner shows a tendency to decrease. The toluene-insoluble matter is determined by placing a polymer component making up the polymerized toner in a 80-mesh woven metal basket, immersing the basket in toluene for 24 hours at room temperature, drying the solids remaining in the basket by a vacuum drier and then measuring the weight of the dry solids to express it in terms of % by weight based on the weight of the polymer component.

The polymerized toner in the present invention has a ratio (r_l/r_s) of the length (r_l) to the breadth (r_s) within a range of 1 to 1.2, and preferably, 1 to 1.15. If the ratio is too high, the resolution of an image formed from such a polymerized toner decreases. In addition, when such a polymerized toner is contained in a toner container in an image forming apparatus, its durability shows a tendency to decrease since the friction between particles of the polymerized toner increases, so external additives, such as a flowability improver, are separated from the toner.

The polymerized toner in the present invention can be used as a developer as it is. However, it may also be used as a developer with various kinds of additives (external additives), such as a flowability improver, added as needed. The additives generally attach to the surface of the polymerized toner. Various kinds of inorganic particles and organic resin particles can be cited as examples of the external additives. Of these, silica particles and titanium oxide particles are preferred, and silica particles subjected to a hydrophobicity-imparting treatment are particularly preferred. In order to attach the external additives to the polymerized toner, normally the external additives and the polymerized toner are charged into a mixer such as a Henschel mixer and stirred.

When the polymerized toner in the present invention is used, the fixing temperature can be lowered to a low temperature of 80 to 150°C, and preferably, 80 to 130°C. In addition, the polymerized toner does not aggregate during its storage and is excellent in shelf-life stability.

Image Forming Apparatus

/31

An image forming apparatus, to which the polymerized toner in the present invention is applied, comprises a photosensitive member (photosensitive drum), a means for charging the surface of the photosensitive member, a means for forming an electrostatic latent image on the surface of the photosensitive member, a means for receiving a toner (developer), a means for supplying the toner to develop the electrostatic latent image on the surface of the photosensitive member to form a toner image, and a means for transferring the toner image from the surface of the photosensitive member to a transfer medium. A specific example of such an image forming apparatus is shown in Figure 1.

As shown in Figure 1, in the image forming apparatus, a photosensitive drum 1 as the photosensitive member is installed rotatably in the direction of an arrow A. The photosensitive drum 1 has a structure that a photoconductive layer is provided around a peripheral surface of an electroconductive support drum. The photoconductive layer is composed of, for example, an organic photosensitive member, selenium photosensitive member, zinc oxide photosensitive member, amorphous silicon photosensitive member, etc.

A charging roll 2 as a charging means, a laser beam irradiating device 3 as a latent image forming means, a developing roll 4 as a developing means, a transfer roll 10 as a transfer means, and, as needed, a cleaning device (not shown) are arranged around the photosensitive drum 1 along the circumferential direction of the drum.

The charging roll 2 is used for evenly charging the surface of the photosensitive drum 1 either positively or negatively. Voltage is applied to the charging roll 2, and the charging roll 2 is brought into contact with the surface of the photosensitive drum 1; hence, the surface of the photosensitive drum 1 is charged. The charging roller 2 may be replaced by a charging means in corona discharge.

The laser beam irradiating device 3 is used for irradiating light corresponding to image signals on the surface of the photosensitive drum 1 to expose the surface of the photosensitive drum 1 evenly charged to the light on the predetermined pattern; hence, an electrostatic latent image is formed in the exposed portion of the drum (in the case of reversal development) or an electrostatic latent image is formed in the unexposed portion of the drum (in the case of normal development). An example of other latent image forming means includes one composed of an LED array and an optical system. /32

The developing roll 4 is used for applying a toner on the electrostatic latent image formed on the surface of the photosensitive drum 1. Bias voltage is applied between the developing roll 4 and the photosensitive drum 1 in such a manner that the toner is applied only to a light-exposed portion of the photosensitive drum 1 in reversal development, or only to a light-unexposed portion of the photosensitive drum 1 in normal development.

The developing roll 4 and a feed roll 6 are arranged in a casing 9 for receiving the toner 7. The developing roll 4 is arranged in the vicinity of the photosensitive drum 1 in such a manner that a part thereof comes into contact with the photosensitive drum 1, and is rotated in a direction B opposite to the rotating direction of the photosensitive drum 1. The feed roll 6 is rotated in contact with and in the same direction

C as the developing roll 4 to supply the toner 7 to the outer periphery of the developing roll 4. An agitating means (agitating blade) 8 for agitating the toner is installed in the casing 9.

A blade 5 for a developing roll as a layer thickness regulating means is arranged in a position between the contact point with the feed roll 6 and the contact point with the photosensitive drum 1 on the periphery of the developing roll 4. The blade 5 is composed of conductive rubber or stainless steel, and voltage of |200 V| to |600 V| normally is applied to the blade to charge the toner. Therefore, the resistivity of the blade 5 is preferably $10^6 \times \Omega$ or lower.

The polymerized toner 7 in the present invention is accommodated in the casing 9 of the image forming apparatus. The polymerized toner 7 may comprise additives, such as a flowability improver, that attaches to it. Since the polymerized toner in the present invention has a core-shell structure, and the shell of the surface layer is formed from a polymer having a relatively high glass transition temperature, the tackiness of the surface is reduced, so the polymerized toner is prevented from aggregating during storage in the casing 9. In addition, since the particle diameter distribution of the polymerized toner in the present invention is relatively sharp, the toner layer formed on the developing roll 4 can be made a substantially single layer by the layer thickness regulating means 5; hence, reproducible images are formed with good quality. /33

The transfer roll 10 serves to transfer the toner image formed on the surface of the photosensitive drum 1 by the developing roll 4 to a transfer medium 11. examples of the transfer medium 1 include paper and resin sheets such as OHP sheets. A corona discharge device and a transfer belt can be cited as transferring means in addition to the transfer roll 10.

The toner image transferred to the transfer medium 11 is fixed to the transfer medium by a fixing means. The fixing means normally is composed of a heating means and a press-bonding means. More specifically, the fixing means normally is composed of a combination of a heating roll (fixing roll) 12 and a press roll 13. The transfer medium 11, to which the toner image has been transferred, is passed between the heating roll 12 and the press roll 13 to melt the toner, and at the same time, it is press-bonded to the transfer medium 11; hence, the toner image is fixed to it.

In the image forming apparatus in the present invention, the polymerized toner in the present invention is used as a toner. Therefore, the toner is easily melted even when the heating temperature by the heating means is low, and is fixed to the transfer medium in a flattened state by slightly pressing it by the press-bonding means; hence, a high-speed printing or copying is possible. Moreover, the toner image fixed to an OHP sheet

is excellent in permeability through an OHP.

The cleaning device is used for cleaning off the toner remaining on the surface of the photosensitive drum 1 without transferring and is composed of, for example, a cleaning blade, etc. It is not always necessary to install the cleaning device when a system for cleaning is conducted by the developing roll 4 at the same time as developing. /34

Image Forming Method

In the image forming method in the present invention, which includes the steps of applying a toner to the surface of a photosensitive member, on which an electrostatic latent image has been formed, to make the latent image visible, and then transferring the visible image to a transfer medium, the polymerized toner in the present invention is used as the toner.

<Practical Examples>

The present invention will now be explained more specifically by citing Practical Examples and Comparative Examples. However, the present invention is not limited to these Practical Examples only. Incidentally, "part(s)" and "%" mean part(s) by weight and wt. % unless expressly noted.

Physical properties in the Practical Examples and Comparative Examples were measured in accordance with the following respective methods.

(1) Particle Diameter of Polymer

The volume average particle diameters (dv) of colored polymer particles (core particles) and polymer particles, and the particle diameter distribution thereof, i.e., the ratio (dv/dp) of the volume average particle diameter to a number average particle diameter (dp) were measured by means of a Multisizer (manufactured by Coulter Co.). The measurement by the Multisizer was conducted under the following conditions:

aperture diameter: 50 μ m; medium: Isothone II; concentration: 15%; and number of particles measured: 50,000 particles.

(2) Thickness of Shell

The thickness of the shell in each toner sample was calculated out in the following equation though it can be measured by the Multisizer or an electron microscope when the shell is thick.

The thickness of shell (μ m) = $dr(1+s/100)^{1/3} - dr$ wherein **dr** is the radius of core particles before addition of a polymerizable monomer /35

for the shell (half of the volume average particle diameter of the core particles found from measurement by the Multisizer), and s is the number of parts of a polymerizable monomer for the shell added (the number of parts per 100 parts by weight of a polymerizable monomer for the core).

(3) Volume Resistivity of Toner

The volume resistivity of each toner sample was measured by means of a dielectric loss measuring device (TRS-10 Model, tradename; manufactured by Ando Electric Co., Ltd.) under conditions of a temperature of 30°C and a frequency of 1 kHz.

(4) Fixing Temperature of Toner

A commercially available printer (4 sheets of paper per minute printer) of a non-magnetic one-component development system was refurbished in such a manner that the temperature of a fixing roll could be varied. This refurbished printer was used to evaluate the toner images. The temperature at which a fixing rate of the toner was 80% was defined as the fixing temperature. The fixing test was conducted by varying the temperature of the fixing roll in the printer to determine the fixing rate at each temperature and find the relationship between the temperature and the fixing rate. The fixing rate was calculated from the ratio of image densities before and after a peeling operation using a pressure-sensitive adhesive tape, which was conducted against a black solid-printed area of a test paper sheet, on which printing had been made by the modified printer. Assuming that the image density before the peeling of the adhesive tape is ID_{before} , and the image density after the peeling of the adhesive tape is ID_{after} , the fixing rate is determined by the following equation:

$$\text{Fixing rate (\%)} = (ID_{\text{after}} / ID_{\text{before}}) \times 100$$

In this test, the black solid-printed area means an area controlled in such a manner that the toner is made to adhere to all dots within this area. The peeling operation of the pressure-sensitive adhesive tape is a series of operations wherein a pressure-sensitive adhesive tape (Scotch Mending Tape 810-3-18, product of Sumitomo 3M, Ltd.) is applied to a measuring area of the test paper sheet to make the tape adhere to the sheet by pressing the tape under a fixed pressure, and the adhesive tape is then peeled at a fixed rate in a direction along the paper sheet. The image density was measured by means of a reflection image densitometer manufactured by McBeth Co.

(5) Shelf-Life Stability of Toner

/36

The evaluation of the shelf-life stability was conducted by placing each toner sample in a closed container to seal it, sinking the container into a constant-temperature water bath controlled to 55°C and then taking the container out of the water bath after a predetermined period of time passed to measure the weight of toner aggregated. The sample taken out of the container was transferred onto a 42-mesh screen so as not to destroy the structure thereof as much as possible, and the screen was vibrated for 30 seconds by means of a powder measuring device, REOSTAT (manufactured by Hosokawa Micron Corp.), with the intensity of vibration preset to 4.5.

Subsequently, the weight of the toner remaining on the screen was measured to get the weight of the toner aggregated. The aggregation rate (wt. %) of the toner was calculated out from this weight of the aggregated toner and the weight of the sample.

The shelf-life stability of the toner sample was evaluated by 4 ranks in accordance with the following standards:

- ⊙: aggregation rate was lower than 5 wt. %;
- : aggregation rate was 5 wt. % or higher but 10 wt. % or lower;
- △: aggregation rate was 10 wt. % or higher but 50 wt. % or lower
- ×: aggregation rate was 50 wt. % or higher.

(6) Permeability through OHP

The temperature of the fixing roll in the refurbished printer described above was set to 150°C to conduct printing with each toner sample on a commercially available OHP sheet (Transparency, product of Uchida Yoko Co., Ltd.) to evaluate the permeability of the sample through an OHP. Whether the printed image permeated through the OHP sheet or not was visually observed to rank it as ○ where the image permeated, or × where the image did not permeate.

(7) Charge Level of Toner

The charge level of each toner sample was measured under respective environments of L/L (10°C in temperature and 20% humidity, RH) and H/H (35°C in temperature and 80% humidity, RH) to evaluate the circumstances under varied environments thereof.

The charge level of the toner was determined in the following manner. The toner was charged into a commercially available printer (4-sheet printer) under each of the above-mentioned environments and left to stand for 24 hours, after which a print pattern of half tone was printed 5 times, and the toner on a developing roll was then sucked in a suction type charge level meter to measure a charge level per unit weight from the charge

/37

level and weight of the toner sucked at this time.

(8) Evaluation of image quality

A continuous printing was conducted from the beginning to count the number of printed sheets that retained an image density of 1.3 or higher as measured by a reflection densitometer (manufactured by McBeth Co) and at an unprinted area, fog of 10% or lower as measured by a whiteness meter (manufactured by Nippon Denshoku K.K.), and image quality was evaluated in accordance with the following standards:

- o: the number of the above-mentioned printed sheets was 10,000 or more;
- Δ: the number of the above-mentioned printed sheets was 5,000 or more but 10,000 or less; and
- ×: the number of the above-mentioned printed sheets was less than 5,000.

[Practical Example 1]

A polymerizable monomer for the core (calculated $T_g=50^{\circ}\text{C}$) comprising 78 parts of styrene and 22 parts of n-butyl acrylate, and 7 parts of carbon black (Printex 150T, trade name; product of Degussa AG), 1 part of a charge control agent (Spiron Black TRH, trade name; product of Hodogaya Chemical Co., Ltd.), 0.3 parts of divinylbenzene, 0.8 parts of a polymethacrylic ester macromonomer (AA6, trade name; $T_g=94^{\circ}\text{C}$; product of Toagosei Chemical Industry Co., Ltd.), 10 parts of pentaerythritol tetrastearate (purity of stearic acid: about 60%) and 4 parts of t-butyl peroxy-2-ethylhexanoate were stirred and mixed at 12,000 rpm in a homomixer (TK type, manufactured by Tokushu Kika Kogyo Co., Ltd.) capable of mixing with high shearing force and uniformly dispersed to obtain a polymerizable monomer composition (liquid mixture) for the core.

Meanwhile, 10 parts of methyl methacrylate (calculated $T_g=105^{\circ}\text{C}$) /38 and 100 parts of water were subjected to a finely dispersing treatment by an ultrasonic emulsifier, thereby obtaining an aqueous dispersion of a polymerizable monomer for the shell. The droplet diameter of the droplets of the polymerizable monomer for the shell was 1.6 μm in terms of D_{90} as determined by means of a microtrack particle diameter distribution measuring device by adding the droplets at a concentration of 3% to a 1% aqueous solution of sodium hexametaphosphate.

On the other hand, an aqueous solution with 6.9 parts of sodium hydroxide (alkali metal hydroxide) dissolved in 50 parts of ion-exchange water was gradually added to an aqueous solution with 9.8 parts of magnesium chloride (water-soluble polyvalent metallic salt) dissolved in 250 parts of ion-exchanged water under stirring to prepare a dispersion of colloid of magnesium hydroxide (colloid of hardly water-soluble metal hydroxide). The particle diameter distribution of the above-mentioned obtained colloid

formed was measured by means of the microtrack particle diameter distribution measuring device (manufactured by Nikkiso Co., Ltd.) and found to be 0.38 μm in terms of D_{50} (50% cumulative value of number particle diameter distribution) and 0.82 μm in terms of D_{90} (90% cumulative value of number particle diameter distribution). The measurement by means of the microtrack particle diameter distribution measuring device was performed under the following conditions:

measuring range: 0.12 to 704 μm ; measuring time: 30 seconds; and medium: ion-exchange water.

The polymerizable monomer composition for the core prepared above was then poured into the colloidal dispersion of magnesium hydroxide obtained above, and the resultant mixture was stirred at 12,000 rpm under high shearing force by means of the TK type homomixer, thereby forming droplets of the polymerizable monomer composition for the core. The aqueous dispersion containing droplets of the monomer composition for the core was charged into a reactor equipped with an agitating blade to initiate a polymerization reaction at 90°C. At the time a conversion into a polymer reached almost 100%, the polymerizable monomer for the shell prepared above and 1 part of a 1% aqueous solution of potassium persulfate were added to continue the reaction for 5 hours. After that, the reaction was stopped to obtain an aqueous dispersion containing polymer particles of core-shell structure.

The volume average particle diameter (d_v) of core particles measured by taking them out just before the polymerizable monomer for the shell was added was 5.7 μm , and a ratio of the volume average particle diameter (d_v) to the number average particle diameter (d_p) thereof was 1.32. The polymer particles had a shell thickness of 0.09 μm and an r_l/r_s ratio of 1.1 and contained 2% of toluene-insoluble matter. /39

The pH of the system was adjusted to 4 or lower with sulfuric acid to conduct acid washing (25°C, 10 minutes) while stirring the above-mentioned obtained aqueous dispersion of the polymer particles of core-shell structure.

After water was separated by filtration from the dispersion, 500 parts of fresh ion-exchange water were added to form a slurry again, and the slurry was washed with water. After that, the dehydration and water washing were repeated several times, and the solids were separated by filtration.

The solids were dried at 45°C for 24 hours with a dryer to obtain polymer particles (polymerized toner).

0.3 parts of colloidal silica (R-972, trade name; product of Nippon Aerosil Co., Ltd.) subjected to a hydrophobicity-imparting treatment were added to 100 parts of the polymerized toner of core-shell structure obtained above, and they were mixed with a Henschel mixer to prepare a non-magnetic one-component developer (simply referred to as developer or toner). The volume resistivity of the toner thus obtained was measured and found to be 11.3 $\log \Omega \cdot \text{cm}$.

Upon measuring the toner obtained above its fixing temperature, it was 120°C. This shelf-life stability of the toner was extremely good (rank=□). In the evaluation of an image, the image density was high, it was free of fog and irregularities, and it was extremely good in resolution. The results are shown in Table 1.

[Practical Example 2]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that the amount of pentaerythritol tetrastearate used in Practical Example 1 was changed to 5 parts. In the evaluation of the image, image density was high, it was free of fog and irregularities, and it was extremely good in resolution. The results are shown in Table 1.

[Practical Example 3]

/40

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that pentaerythritol tetrastearate used in Practical Example 1 was changed to glycerol triarachidate (purity of arachidic acid: about 60%). The results are shown in Table 1.

[Comparative Example 1]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that pentaerythritol tetrastearate used in Practical Example 1 was changed to paraffin wax having a melting point of 60°C. The results are shown in Table 1.

[Comparative Example 2]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that pentaerythritol tetrastearate used in Practical Example 1 was changed to low molecular weight polypropylene having a number average molecular weight of 2,200. The results are shown in Table 1.

Table 1

	Practical Examples			Comparative Examples	
	1	2	3	1	2
Core particles					
dv [μm]	5.7	5.7	6.1	6.5	6.0
dv/dp	1.32	1.28	1.25	1.35	1.22
Polymer particles					
Shell thickness [μm]	0.09	0.09	0.09	0.10	0.10
Toluene-insoluble matter [%]	2	3	3	2	4
Toner evaluation					
dv [μm]	5.9	5.9	6.3	6.7	6.2
dv/dp	1.30	1.30	1.28	1.36	1.24
Volume resistivity [$\log \Omega \text{ cm}$]	11.3	11.4	11.2	11.0	11.4
Fixing temperature [$^{\circ}\text{C}$]	120	130	130	150	160
Shelf-life stability	◎	◎	◎	△	△
L/L charge level [$\mu\text{c/g}$]	-26	-24	-28	25	-27
H/H charge level [$\mu\text{c/g}$]	-16	-25	-25	-20	-25
Evaluation of image quality	○	○	○	×	△

[Comparative Example 3]

4 parts of saturated polyester, 83 parts of styrene, 17 parts of butyl acrylate, 7 parts of carbon black, 1 part of a metal compound of salicylic acid and 10 parts of pentaerythritol dibehenate diacetate were dispersed by the TK type homomixer, and 5 parts of 2,2'-azobis(2,4-dimethylvaleronitrile) were added to the dispersion to prepare a polymerizable monomer composition. After the polymerizable monomer composition was granulated, it was heated to 60°C to conduct polymerization for 10 hours. After the polymerization, it was washed and dried to obtain polymer particles (polymerized toner). A developer (toner) was obtained in the same manner as in Practical Example 1 except that this polymerized toner was used.

The results are shown in Table 2.

[Practical Example 4]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 10 parts of methyl methacrylate used as the polymerizable monomer for the shell in Practical Example 1 were changed to 9 parts of methyl methacrylate and 1 part of butyl acrylate. The results are shown in Table 2.

[Practical Example 5]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 10 parts of styrene were used instead of 10 parts of methyl methacrylate used as the polymerizable monomer for the shell in Practical Example 1, and 20 parts of methanol were added just before the polymerizable monomer for the shell was added. The results are shown in Table 2.

[Practical Example 6]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 2,2-azobisisobutyronitrile was used instead of t-butyl peroxy-2-ethylhexanoate used as the polymerization initiator for the polymerizable monomer for the core in Practical Example 1, and the reaction temperature was changed to 75°C. The results are shown in Table 2. When this developer was used to conduct fixing, a slight odor was given off.

[Practical Example 7]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that the polymerizable monomer for the shell was added without conducting the treatment by means of the ultrasonic emulsifier in Practical Example 1. The results are shown in Table 2.

Table 2

	Practical Example				Comparative Example
	4	5	6	7	3
Core particles					
dv [μm]	6.0	6.1	5.9	6.5	6.2
dv/dp	1.27	1.31	1.35	1.40	1.38
Polymer particles					
Shell thickness [μm]	0.10	0.10	0.09	0.10	0.09
Toluene-insoluble matter [%]	3	3	5	4	4
Toner evaluation					
dv [μm]	6.2	6.3	6.1	6.7	6.4
dv/dp	1.27	1.31	1.33	1.40	1.37
Volume resistivity [$\log \Omega \text{ cm}$]	11.3	11.4	11.2	11.1	11.1
Fixing temperature [$^{\circ}\text{C}$]	120	130	130	130	140
Shelf-life stability	◎	◎	◎	○	×
L/L charge level [$\mu\text{c/g}$]	-27	-30	-22	-23	-20
H/H charge level [$\mu\text{c/g}$]	-22	-27	-18	-19	-17
Evaluation of image quality	○	○	○	○	×

[Practical Example 8]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that butyl acrylate used as the polymerizable monomer for the core in Practical Example 1 was changed to 2-ethylhexyl acrylate. The results are shown in Table 3.

[Practical Example 9]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 5 parts of a magenta pigment (Pigment Red 122) were used instead of 7 parts of the carbon black used in Practical Example 1. The results are shown in Table 3.

/44

[Practical Example 10]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 5 parts of a yellow quinophthalone pigment (Pigment Yellow 138) were used instead of 7 parts

of the carbon black used in Practical Example 1. The results are shown in Table 3.

[Practical Example 11]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that 5 parts of a cyan pigment (Pigment Blue 15:3) were used instead of 7 parts of the carbon black used in Practical Example 1. The results are shown in Table 3.

[Comparative Example 4]

A polymerized toner and a developer (toner) were obtained in the same manner as in Comparative Example 1 except that 5 parts of a magenta pigment (Pigment Red 122) were used instead of 7 parts of the carbon black used in Practical Example 1. The results are shown in Table 3.

/45

Table 3

	Practical Example				Comparative Example
	8	9	10	11	4
Core particles					
dv [μm]	6.3	6.1	6.2	6.5	5.9
dv/dp	1.21	1.18	1.25	1.31	1.27
Polymer particles					
Shell thickness [μm]	0.10	0.10	0.10	0.10	0.09
Toluene-insoluble matter [%]	3	4	5	6	4
Toner evaluation					
dv [μm]	6.5	6.3	6.4	6.7	6.1
dv/dp	1.22	1.17	1.24	1.29	1.27
Volume resistivity [$\log \Omega \text{ cm}$]	11.4	12.5	12.4	11.6	12.4
Fixing temperature [$^{\circ}\text{C}$]	120	130	120	130	130
Shelf-life stability	◎	◎	◎	◎	△
L/L charge level [$\mu\text{c/g}$]	-28	-32	-34	-28	-33
H/H charge level [$\mu\text{c/g}$]	25	30	31	25	29
OHP permeability	-	○	○	○	○
Evaluation of image quality	○	○	○	○	×

[Practical Example 12]

A polymerized toner and a developer (toner) were obtained in the same manner as in Practical Example 1 except that pentaerythritol tetramyristate was used instead of the pentaerythritol tetrastearate used in Practical Example 1.

The volume average particle diameter (d_v) of the core particles measured by taking them out just before the polymerizable monomer for the shell was added was $5.8 \mu\text{m}$, and a ratio of the volume average particle diameter (d_v) to the number average particle diameter (d_p) thereof was 1.22. /46 The polymer particles had a shell thickness of $0.09 \mu\text{m}$ and an r_l/r_s ratio of 1.1 and contained 2% of toluene-insoluble matter.

The volume resistivity of the non-magnetic one-component developer (toner) obtained by adding colloidal silica subjected to the hydrophobicity-imparting treatment to the polymerized toner was $11.3 \log \Omega \cdot \text{cm}$. The toner was used to measure the fixing temperature, which was 120°C . The shelf-life stability of the toner was extremely good (rank=□). The toner had charge levels of $-28 \mu\text{c/g}$ and $-25 \mu\text{c/g}$ under L/L and H/H environments, respectively. The evaluation of image revealed that an image high in image density, free of fog and irregularities, and extremely good in resolution was obtained (rank of image quality=○).

Moreover, the solubility of the pentaerythritol tetramyristate in the polymerizable monomer was more superior than pentaerythritol tetrastearate, and so there was no need to grind or melt it in advance to improve the solubility at room temperature.

<Industrial Applicability>

In the present invention, polymerized toners which have a low fixing temperature and uniformly melting ability, and moreover are excellent in shelf-life stability, and a method of manufacture thereof are obtained.

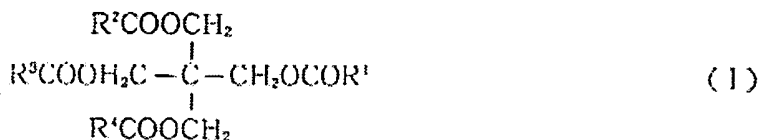
In the present invention, polymerized toners which have excellent offset resistance, shelf-life stability and flowability, can meet high-speed printing at a low fixing temperature, can achieve high resolution and are suitable for use as color toners, and a method of manufacture thereof are obtained. The use of the polymerized toners in the present invention permits the copying or printing at higher speeds, the formation of full-color images and energy savings. The polymerized toners in the present invention can form toner images which exhibit excellent permeability when doing printing on an OHP sheet and fixing the resulting image to it. The polymerized toners in the present invention allow the formation of high-quality images without causing fogging and deterioration of the image density. In the present invention, an image forming method using the polymerized toner(s) having such excellent various properties, and an

image forming apparatus in which the polymerized toner(s) are accommodated.

Claim(s)

/47

1. A polymerized toner of core-shell structure, comprising core particles composed of colored polymer particles, which comprise a polyfunctional ester compound formed from a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, and a colorant, and a shell which is formed from a polymer having a glass transition temperature higher than that of a polymer component making up the core particles and covers each of the core particles.
2. The polymerized toner of Claim 1 wherein the core particles are colored polymer particles obtained by subjecting a polymerizable monomer composition containing a polymerizable monomer for the core, the polyfunctional ester compound formed of the polyhydric alcohol and the carboxylic acid, and the colorant to suspension polymerization.
3. The polymerized toner in Claim 1 wherein the core particles are colored polymer particles obtained by subjecting a polymerizable monomer composition containing a polymerizable monomer for the core, the polyfunctional ester compound formed from the polyhydric alcohol and the carboxylic acid, and the colorant to suspension polymerization in the presence of a macromonomer.
4. The polymerized toner in Claim 1 wherein the shell is a polymer layer formed on the core particle surface by subjecting a polymerizable monomer for the shell to suspension polymerization in the presence of the core particles.
5. The polymerized toner of Claim 1 wherein the average particle size of the core particles is 0.5 to 20 μm and the average thickness of the shell is 0.001 to 1 μm .
6. The polymerized toner of Claim 1 wherein the volume average molecular weight is 2 to 20 μm and the particle diameter distribution (volume average particle diameter/number average particle diameter) is 1.6 or less. /48
7. The polymerized toner in Claim 1 wherein the polyfunctional ester compound is contained in a proportion of 0.1 to 40 parts by weight per 100 parts by weight of the polymer component making up the core particles.
8. The polymerized toner of claim 1 wherein the polyfunctional ester compound is a compound represented by the formula (I):



(where R^1 , R^2 , R^3 and R^4 are an alkyl group or phenyl group, respectively, and the number of carbon atoms in the alkyl group or phenyl group is 10 to 30.)

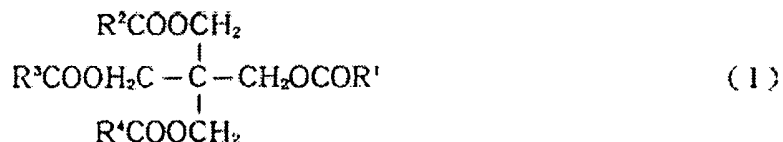
9. The polymerized toner of Claim 8 wherein the polyfunctional ester compound is pentaerythritol tetrastearate or pentaerythritol tetramyristate.

10. A method for manufacturing a polymerized toner of core-shell structure which comprises the steps of (1) subjecting a polymerizable monomer composition containing a polyfunctional ester compound formed from a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, a colorant, and a polymerizable monomer for the core, which is capable of forming a polymer having a glass transition temperature of 80°C or lower, to suspension polymerization in an aqueous dispersion medium containing a dispersing agent to prepare core particles formed of colored polymer particles and then (2) subjecting a polymerizable monomer for the shell, which is capable of forming a polymer having a glass transition temperature higher than that of a polymer component making up the core particles, to suspension polymerization in the presence of the core particles, thereby forming shell which is formed of a polymer layer /49 and covers each of the core particles.

11. The method of manufacture in Claim 10 wherein, in the step (1), the polymerizable monomer composition is subjected to the suspension polymerization in the presence of a macromonomer to prepare core particles formed from colored polymer particles.

12. The method of manufacture of Claim 10 wherein the polyfunctional ester compound content is 0.1 to 40 parts by weight per 100 parts by weight of the polymerizable monomer for the core.

13. The method of manufacture of claim 11 wherein the polyfunctional ester compound is a compound represented by the formula (I):



(where R^1 , R^2 , R^3 and R^4 are an alkyl group or phenyl group, respectively, and the number of carbon atoms in the alkyl group or phenyl group is 10 to 30.)

14. The method of manufacture of Claim 13 wherein the polyfunctional ester compound is pentaerythritol tetrastearate or pentaerythritol tetramyristate.

15. The method of manufacture of Claim 10 wherein the polymerizable monomer composition further contains a crosslinkable monomer.

16. The method of manufacture of claim 11 wherein the macromonomer /50 has a number average molecular weight of 1,000 to 30,000 and has a glass transition temperature higher than the glass transition temperature of the monomer obtained by polymerizing the polymerizable monomer for the core.

17. The method of manufacture of Claim 11 wherein the amount of the macromonomer used is 0.01 to 10 parts by weight per 100 parts by weight of polymerizable monomer for the core.

18. The method of manufacture of Claim 10 wherein, in step (1), the polymerizable monomer composition is subjected to suspension polymerization using an oil-soluble radical polymerization initiator in an aqueous dispersion medium.

19. The method of manufacture of Claim 18 wherein the oil-soluble radical polymerization initiator is an organic peroxide whose ten-hour half-life temperature is 60 to 80°C and molecular weight is 250 or lower.

20. The method of manufacture of Claim 10 wherein, in step (1), a suspension polymerization is performed in an aqueous dispersion medium containing a colloid of a hardly water-soluble metal hydroxide as a dispersing agent.

21. The method of manufacture of Claim 20 wherein the colloid of a hardly water-soluble metal hydroxide has number particle diameter distributions D_{50} of at most 0.5 μm (50% cumulative value of number particle diameter distribution) and D_{90} (90% cumulative value of number particle diameter distribution) of at most 1 μm .

22. The method of manufacture of Claim 20 wherein the colloid of a /51 hardly water-soluble metal hydroxide is a colloid of a hardly water-soluble metal hydroxide obtained by bringing the pH of the aqueous solution of the water-soluble polyvalent metal compound to 7 or higher.

23. The method of manufacture of Claim 20 wherein the colloid of a hardly water-soluble metal hydroxide is a colloid of a hardly water-soluble metal

hydroxide obtained by allowing a water-soluble polyvalent metal compound and an alkali metal hydroxide in a water phase.

24. The method of manufacture of 10 wherein, in the step (1), wherein a solution mixture containing at least a polyfunctional ester compound, polymerizable monomer for a core, and a radical polymerization initiator is prepared, then this solution mixture is charged into an aqueous dispersion medium containing a dispersing agent, stirred and granulated to minute droplets, after which it is subjected to a suspension polymerization at a temperature of 30 to 200°C.

25. The method of manufacture of Claim 10 wherein, in step (1), core particles comprising colored polymer particles whose volume average particle diameter (dv) is 0.5 to 20 μm and the ratio (dv)/(dp) of the volume average particle diameter (dv) to a number average particle diameter (dp) is at most 1.7 are prepared

26. The method of manufacture of Claim 10 wherein, in step (2), the polymerizable monomer for the shell are subjected to a suspension polymerization as droplets having a number average particle diameter smaller than the core particles.

27. The method of manufacture of Claim 10 wherein the polymerizable monomer for the shell is a monomer with a solubility in 20°C water of 0.1 wt. %.

28. The method of manufacture of Claim 10 wherein the polymerizable /52 monomer for the shell is a monomer with a solubility in 20°C water less than 0.1 wt. %, and in the step (2), a suspension polymerization is conducted by adding said polymerizable monomer for the shell and an organic solvent with a solubility in 20°C water of 0.5 wt. % or higher.

29. The method of manufacture of Claim 10 wherein, in step (2), a suspension polymerization is conducted by adding the polymerizable monomer for the shell and a charge control agent.

30. The method of manufacture of Claim 10 wherein, in step (2), the polymerizable monomer for the shell is subjected to a suspension polymerization with a water-soluble radical polymerization initiator.

31. The method of manufacture of Claim 10 wherein, in step (2), wherein the shell comprising a polymer layer with a 0.001 to 1 μm average coating thickness.

32. An image forming method comprising the steps of applying a toner to the surface of a photosensitive member, on which an electrostatic latent image has been formed, to make the latent image visible, and then transferring the visible image onto a transfer medium; said image forming method

characterized by using, a the toner, a polymerized toner with a core-shell structure wherein core particles composed of colored polymer particles, which comprise a polyfunctional ester compound formed of a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, and a colorant, and shell which is formed of a polymer having a glass transition temperature higher than that of a polymer component making up the core particles and covers each of the core particles is provided.

33. An image forming apparatus containing a photosensitive member, a means for charging the surface of the photosensitive member, a means for forming an electrostatic latent image on the surface of the photosensitive member, a means for receiving a toner, a means for supplying said toner /53 to develop the electrostatic latent image on the surface of the photosensitive member, and form a toner image, and a means for transferring said toner image from the surface of the photosensitive member to a transfer medium; said image forming apparatus characterized by the means for receiving the toner containing the polymerized toner with a core-shell structure wherein core particles composed of colored polymer particles, which comprise a polyfunctional ester compound formed of a trifunctional or higher polyfunctional polyhydric alcohol and a carboxylic acid, and a colorant, and a shell which is formed from a polymer having a glass transition temperature higher than that of a polymer component making up said core particles and covers each of core particles.

Figure 1

